

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
2 October 2003 (02.10.2003)

PCT

(10) International Publication Number  
WO 03/080708 A1

- (51) International Patent Classification: C08G 73/02, 1101B 1/12
- (21) International Application Number: PCT/IN02/00058
- (22) International Filing Date: 21 March 2002 (21.03.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (71) Applicant: COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH [IN/IN]; Rafi Marg, New Delhi 110 001 (IN).
- (72) Inventors: PALANIAPPAN, Srinivasan; Indian Institute of Chemical Technology, Hyderabad 500 007, Andhra Pradesh (IN). CHELLACHAMY, Anbalagan, Amar-nath; Indian Institute of Chemical Technology, Hyderabad 500 007, Andhra Pradesh (IN).
- (74) Agents: HARIHARAN, Subramaniam et al.; Subramaniam, Nataraj & Associates, E 556 Greater Kailash II, New Delhi 110 048 (IN).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE PREPARATION OF POLYANILINE SALT

(57) Abstract: The present invention provides a process for preparing electrically conductive polyaniline salts in various organic solvents using cost-effective protonic acids and where the solution is optically transparent.

WO 03/080708 A1

## PROCESS FOR THE PREPARATION OF POLYANILINE SALT

### Field of the invention

The present invention relates to a process for the preparation of a polyaniline salt in organic solvents. More particularly, the present invention relates to a process for preparing electrically conductive polyaniline salts in various organic solvents using cost-effective protonic acids and where the solution is optically transparent.

### Background of the invention

A lot of research work in the area of electrically conductive polymers is being carried out at the moment all over the world. These polymers make it possible to replace metallic conductors and semi-conductors in many applications such as batteries, transducers, switches, solar cells, circuit boards, heating elements and in electrostatic discharge (ESD) and electromagnetic interference shielding (EMI) applications. The advantages of electrically conductive polymers compared to metals are, for instance, their low weight, good mechanical properties, resistance to corrosion and cheaper synthesis and processing methods.

Examples of kinds of inherently electrically conductive polymers are polyacetylene, poly-p-phenylene, polypyrrole, polythiophene and polyaniline. An advantage with an inherently electrically conductive polymers is that its electrical conductivity is easily varied as a function of the doping time, which is especially seen in the case of low conductivities. It is difficult to obtain low conductivities for filled electrically conductive plastics.

Polyaniline has emerged as one of the promising conducting polymers and can be used in a variety of applications, such as paint, anti-static protection, electromagnetic protection, electro-optic devices such as liquid crystal devices (LCDs) and photocells, transducers, circuit boards, etc. However, processing of polyaniline into useful products or devices as described above has been problematic because of its insolubility in common solvents.

Synthesis of polyaniline is commonly performed by the method of chemical oxidative polymerization based upon the aqueous solution polymerization system. (see Cao et al., Polymer, 30:2305, 1989). Typically, polyaniline is produced as solid emeraldine salt from chemical oxidative polymerization in the presence of protonic acids such as HCl and H<sub>2</sub>SO<sub>4</sub>. The polyaniline obtained in such way is normally insoluble, which hinders the application of the polyaniline.

Smith et al., U.S. Pat. No. 5,470,505, disclosed that the emeraldine salt prepared by standard methods of oxidative polymerization of aniline monomer in the presence of a protonic acid can be dissolved in an acid, particularly, in strong acids such as concentrated

H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>SO<sub>3</sub>H, ClSO<sub>3</sub>H, CF<sub>3</sub>SO<sub>3</sub>H and HNO<sub>3</sub> (70% or fuming). The emeraldine salt (polyaniline) dissolved in one of these acid solutions is then processed into desired articles for various applications.

Abe et al., U.S. Pat. No. 5,728,321, disclosed that a solution of polyaniline (dissolved in an aprotic polar solvent, such as N-methyl-2-pyrrolidone) in doped state can be obtained by a method using a specific protonic acid, such as hydrofluoroboric acid, hydrofluorophosphoric acid, perchloric acid, or any other organic acids having acid dissociation constant pK<sub>a</sub> values of less than 4.8, as dopants in the oxidative polymerization of aniline monomer. Also, the polyaniline obtained according to the above method, which is insoluble in an organic solvent, can be dissolved in an aprotic polar solvent, when the polyaniline is in an undoped state. The undoping of doped polyaniline in order to permit the polyaniline to be soluble in organic solvent is burdensome and increases the production cost.

To improve the processability, emulsion polymerization processes for preparing a polyaniline salt of a protonic acid have been reported. (Cao et al., U.S. Pat. No. 5,232,631, Example 6B, 1993; Cao and Jan-Erik, WO94/03528, 1994 I; Cao and Jan-Erik, U.S. Pat. No. 5,324,453, 1994 II; see also, Osterholm et al., P. Synthetic Metals 55:1034-9, 1993). In these disclosures aniline, a protonic acid, and an oxidant were combined with a mixture of polar liquid, typically water and a non-polar or weakly polar liquid, e.g. xylene, chloroform, toluene, decahydronaphthalene and 1,2,4-trichlorobenzene, all of which are either sparingly soluble or insoluble in water.

Smith et al (Polymer 35, 2902, (1994)) reported the polymerization of aniline in an emulsion of water and a non-polar or weakly polar organic solvent. This polymerization was carried out in the presence of a functionalized protonic acid such as dodecylbenzenesulfonic acid, which simultaneously acted as a surfactant and protonating agent for the resulting polyaniline. The resultant polyaniline has a good solubility in non-polar solvents.

Protonic acid primary dopants are described as acting as surfactants because they are purportedly compatible with organic solvents and also enable intimate mixing of the polyaniline in bulk polymers (Cao et al, Synthetic Metals 48:91-97, 1992; Cao et al, U.S. Pat. No. 5,232,631, 1993 which are incorporated by reference). Thus, any surfactant aspect of the primary dopants was thought to contribute to the processability rather than the conductivity of the polyaniline.

Heeger's group (Synthetic Metals 48, 91, 1992); Synthetic Metals 3514 (1993) reported that emeraldine base doped with a functionalized protonic acid, for example,

camphorsulfonic acid and dodecylbenzene sulfonic acid, can be dissolved in a non-polar or moderately-polar organic solvent. This three component system has good solubility in common organic solvents and is compatible with many of the classical polymers.

In our pending Indian patent application No. 1029/DEL/2000, a process for preparation of polyaniline salts is reported. The polyaniline salt is in a carrier organic solvent such as chloroform, dichloromethane, toluene and the solution is optically transparent. Polyaniline salt in carrier organic solvent was prepared via emulsion polymerization pathway by oxidizing aniline to polyaniline salt using benzoyl peroxide as oxidizing agent (benzoyl peroxide is soluble in the above mentioned solvents i.e., chloroform, dichloromethane, toluene).

Benzoyl peroxide is not soluble in most of the other organic solvents such as propanol, butanol, decanol, dodecanol, cyclohexanol, dioctyl phthalate etc. and therefore, emulsion polymerization method for the preparation of polyaniline salt can not be carried out using benzoyl peroxide in the above solvents.

#### 15 **Objects of the invention**

The main object of the present invention is to provide a process for the preparation of polyaniline salts in organic solvents such as N,N-dimethylformamide, dimethyl sulfoxide, N-methyl-2-pyrrolidone, butanol, decanol, dodecanol, cyclohexanol, methylcyclohexane and dioctyl phthalate.

20 The other object of the present invention is to provide a process for the preparation of electrically conducting polyaniline salt in various organic solvents using cost-effective protonic acid such as sulfuric, nitric, hydrochloric acid.

The further object of the present invention is to provide for a process for preparation of polyaniline salt soluble in organic solvents for improved processibility.

25 These and other objects of the invention are achieved and the problems associated with the prior art are overcome by the process of the invention described in detail below.

#### **Summary of the invention**

In the present invention, a process for preparation of polyaniline salts in various organic solvents such as N,N-dimethylformamide, dimethyl sulfoxide, N-methyl-2-pyrrolidone, butanol, decanol, dodecanol, cyclohexanol, methylcyclohexane and dioctyl phthalate has been developed. Accordingly, the process in the present invention comprises of polymerizing aniline in the presence of a mixture of aqueous and hydrocarbon solvent and in the presence of an anionic or a cationic surfactant and radical initiator at a temperature ranging between 30°C to

40°C for at least 24 hours, separating the polyaniline salt in the hydrocarbon solvent by conventional method from the reaction mixture. The hydrocarbon solvent containing polyaniline salt is then mixed with other organic solvents and thereupon the hydrocarbon solvent is evaporated, obtaining polyaniline salt in various organic solvents.

5 In an embodiment of the present invention, the hydrocarbon solvent used is a chlorinated solvent such as dichloromethane, chloroform.

In another embodiment of the present invention, the anionic surfactant used is selected from sodium lauryl sulfate, dioctyl sodium sulfosuccinate and the cationic surfactant used is cetyltrimethylammonium bromide.

10 In yet another embodiment of the present invention, the radical initiator used is benzoyl peroxide.

In still yet another embodiment of the present invention, the protonic acid used is selected from sulfuric acid, nitric acid, hydrochloric acid.

15 In still yet another embodiment of the present invention, the organic solvent used is selected from a group consisting of benzene, toluene, xylene, 1,2-dichlorobenzene, nitro benzene, N,N-dimethylformamide, dimethyl sulfoxide, N-methyl-2-pyrrolidone, butanol, decanol, dodecanol, cyclohexanol, methylcyclohexane and dioctyl phthalate.

In a feature of the present invention, the separation of polyaniline salt in organic solvent may be effected by pouring the reaction mixture into water.

20 In another feature of the invention, the separation of the polyaniline salt from the reaction mixture may be carried out by filtration.

### **Detailed description of the invention**

25 Polyaniline is today one of the most promising conducting polymers and has a wide applicability. Synthesis of polyaniline is normally carried out by the method of chemical oxidative polymerization in the presence of protonic acids such as HCl and H<sub>2</sub>SO<sub>4</sub> based upon the aqueous polymerization system. Usually polyaniline is produced as a solid emeraldine salt, and polyaniline obtained in such way is normally insoluble, which hinders the application of polyaniline. Even if the salt is processed in a manner so that it is soluble in a few solvents the method and the reactants used are not cost-efficient.

30 The present invention relates to a process wherein the polyaniline produced is soluble in organic solvents and the process utilizes cost-efficient protonic acids. The process comprises of polymerizing aniline in the presence of a mixture of an aqueous and a hydrocarbon solvent and in the presence of an anionic or a cationic surfactant and radical

initiator at a temperature ranging between 30°C to 40°C for a period of atleast 24 hours, followed by separating the polyaniline salt in the hydrocarbon solvent by conventional method such as filtration from the reaction mixture. It also may be separated out by pouring the reaction mixture into water. The hydrocarbon solvent containing polyaniline is then mixed  
5 with other organic solvents and the hydrocarbon solvent is evaporated, resulting in the polyaniline salt in an organic solvent.

The invention will now be described in greater detail with reference to the following examples, which are illustrative and therefore should not be construed as limiting the scope of the present invention in any manner:

#### 10 **Example 1**

The following example illustrates the preparation of polyaniline salts.

Sodium lauryl sulfate (2.0 g) is dissolved in 40 ml of distilled water and mixed with a solution containing 4.85 g benzoyl peroxide in 60 ml dichloromethane. The milky-white emulsion thus formed is mechanically stirred at 35°C. Solution containing aniline (2.4 ml) and  
15 sulfuric acid (6.0 ml) in 100 ml of water is added dropwise to the above mixture over a period of approximately 20 minutes. The reaction is allowed to proceed for 24 hours. The color of the emulsion at this time becomes green. The reaction mixture is separated into two layers, separated the bottom oily green phase containing the polyaniline salt and a upper aqueous phase. The upper aqueous phase is removed with a separating funnel and 1500 ml water is  
20 added to the green phase, again the aqueous phase is removed and the green polyaniline salt phase is subsequently washed three times with 1500 ml portions of water. Sodium sulfate (5 g) is added to the polyaniline phase and filtered through filter paper. The polyaniline phase thus obtained is appeared to be uniform to the naked eye and the polymer remained solubilized in the organic phase.

25 Using the above procedure, polyaniline salt systems may also be prepared by using the following variables

- (1) Hydrochloric acid (18 ml) instead of sulfuric acid
- (2) Nitric acid (12 ml) instead of sulfuric acid
- (3) Dioctyl sodium sulfosuccinate (2.0 g) instead of sodium lauryl sulfate
- 30 (4) Cetyltrimethylammonium bromide (2.0 g) instead of sodium lauryl sulfate
- (5) Chloroform solvent (60 ml) instead of dichloromethane

**Example 2**

The following example illustrates the preparation of the polyaniline salts in various organic solvents.

Polyaniline salt in dichloromethane or chloroform solution (1 ml) prepared using example 1 is added to 9 ml of dichloromethane and this solution is mixed with 10 ml of N-methyl-2- pyrrolidone. The solvent dichloromethane is evaporated using Rotavapor and polyaniline salt is transferred to N-methyl-2-pyrrolidone. The solubility of the polyaniline salt in N-methyl-2- pyrrolidone is checked and found to be optically transparent.

**Table 1: Solubility of polyaniline salt in various organic solvents**

Sl.No.	Solvents	Solubility
1	Benzene	Soluble
2	Toluene	Soluble
3	Xylene	Soluble
4	Chlorobenzene	Soluble
5	1,2-dichloro benzene	Soluble
6	Nitro benzene	Soluble
7	N,N-Dimethylformamide	Soluble
8	Dimethyl sulfoxide	Soluble
9	N-methyl-2- pyrrolidone	Soluble
10	Butanol	Soluble
11	Decanol	Soluble
12	Dodecanol	Soluble
13	Cyclohexanol	Soluble
14	Methyl cyclohexane	Soluble
15	Diocetyl phthalate	Soluble
16	Ethylene glycol	Not soluble
17	Tetrahydrofuran	Not soluble
18	2-butoxy ethanol	Not soluble
19	Methanol	Not soluble
20	Ethanol	Not soluble
21	Isoamyl alcohol	Not soluble
22	Paraffin oil	Not soluble

**Example 3**

The following example illustrates the process for the maximum solubility of the polyaniline salts in various solvents.

Polyaniline salt in dichloromethane solution (known amount) is added in to known amount of dichloromethane (the amount of polyaniline salt in dichloromethane is varied from 1ml to 10 ml in steps of 1 ml and the total volume of dichloromethane is kept at 10 ml) and this solution is mixed with 10 ml of N-methyl-2-pyrrolidone. The solvent dichloromethane is

evaporated using Rotavapor and polyaniline salt is transferred to N-methyl-2-pyrrolidone. The solubility of the polyaniline is checked and found to be optically transparent. Similar procedure was used for other test solvents.

**Table 2: Maximum solubility of polyaniline salt in various solvents**

Sl.No.	Solvents	Maximum amount of polyaniline salt in 10 ml of solvent
1	Benzene	8 ml
2	Toluene	8 ml
3	Xylene	8 ml
4	Chlorobenzene	6 ml
5	1,2-dichloro benzene	6 ml
6	Nitro benzene	6 ml
7	N,N-Dimethylformamide	4 ml
8	Dimethyl sulfoxide	6 ml
9	N-methyl-2-pyrrolidone	6 ml
10	Butanol	2 ml
11	Decanol	2 ml
12	Dodecanol	2 ml
13	Cyclohexanol	2 ml
14	Methyl cyclohexane	4 ml
15	Diocyl phthalate	4 ml

5

#### Example 4

The following example illustrates the preparation of the polyaniline salts in mixture of various solvents.

10 Polyaniline salt in dichloromethane solution (known amount) was added in to known amount of dichloromethane (total volume 10 ml) and this solution was mixed with 10 ml of N-methyl-2-pyrrolidone. The solubility of the polyaniline salt in the mixture of solvents is checked and found to be optically transparent. Similar procedure was used for other test solvents.

#### Example 5

15 The following example illustrates the electronic absorption results of the polyaniline salts in various solvents.

The isolated polyaniline salt samples are analyzed by electronic absorption spectral technique using Hitachi U 2000 spectro photo meter. Electronic absorption spectra of



polyaniline salt in organic solvent according to Examples 1 – 3 are recorded and three peaks are observed at around 325-380, 450-540 and 700-850 nm which corresponds to polyaniline salt system.

#### Example 6

The following example illustrates the preparation of the polyaniline salt in the powder form by the emulsion polymerization pathway.

The organic layer obtained in Example 1 which contains polyaniline salt in organic solvent is poured into 500 ml of acetone. Polyaniline salt is thus precipitated out from the organic solvent. The precipitate is then recovered by filtration and the solid is washed with 2000 ml of distilled water followed by 250 ml of acetone. The powder is dried at 100°C, till the constant mass is reached.

The polyaniline salts in the dry powder form are compressed into pellets using a 16 mm diameter Macro-Micro KBr die and a 12-ton laboratory hydraulic press. The powder is placed in the die and a pressure of 2000 lbs is applied. Each pellet thus formed is measured to determine its diameter and thickness. The pellets are in the shape of disks. In measuring the conductivity a pellet is coated with silver paint on both the sides having the same cross sectional area and the resistance is measured using an ohmmeter. Lead resistance is 0.03 Ohms for the pellets. Conductivity is calculated using the following formula:

$$\text{Conductivity} = (\text{Thickness})/(\text{resistance} \times \text{area}) = d/(RA)$$

The conductivity of the polyaniline salt prepared with different acids such as sulfuric, nitric, and hydrochloric acid is found to be 0.1, 0.2, and 0.1 S/cm respectively.

**We Claim:**

1. A process for the preparation of a polyaniline salt comprising
  - (a) polymerizing aniline in the presence of mixture of aqueous and a hydrocarbon solvent, a protonic acid and a radical initiator at a temperature ranging between 30°C to 40°C for a period of at least 24 hours;
  - (b) separating the polyaniline salt in the hydrocarbon solvent from the reaction mixture;
  - (c) mixing the hydrocarbon solvent containing polyaniline salt with one or more other organic solvent and
  - (d) evaporating the hydrocarbon solvent, and obtaining polyaniline salt.
2. A process as claimed in claim 1, wherein the protonic acid is selected from the group consisting of sulfuric acid, nitric acid and hydrochloric acid.
3. A process as claimed in claim 1, wherein the hydrocarbon solvent used in step (b) is a chlorinated solvent selected from dichloromethane and chloroform.
4. A process as claimed in claim 1 wherein the polymerisation is carried out in the presence of an anionic surfactant or a cationic surfactant.
5. A process as claimed in claim 4, wherein the anionic surfactant used is selected from sodium lauryl sulfate and dioctyl sodium sulfosuccinate.
6. A process as claimed in claim 4 wherein the cationic surfactant is cetyltrimethylammonium bromide.
7. A process as claimed in claim 1, wherein the radical initiator used is benzoyl peroxide.
8. A process as claimed in claim 1, the solvent used is selected from the group consisting of benzene, toluene, xylene, chlorobenzene, 1,2-dichlorobenzene, nitro benzene, dimethyl sulfoxide, N-methyl-2- pyrrolidone, butanol, decanol, dodecanol, cyclohexanol, methylcyclohexane, dioctyl phthalate and any mixture thereof.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IN 02/00058

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G73/02 H01B1/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 567 356 A (KINLEN PATRICK J) 22 October 1996 (1996-10-22) claims 1,3 ---	1-8
A	US 5 276 112 A (MANOHAR SANJEEV K ET AL) 4 January 1994 (1994-01-04) claims 1,9,10 ---	1-8
A	WO 93 22775 A (ALLIED SIGNAL INC) 11 November 1993 (1993-11-11) claim 1 ---	1-8
A	EP 0 579 027 A (NITTO DENKO CORP) 19 January 1994 (1994-01-19) claims 1,5 --- -/-	1-8

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\*Z\* document member of the same patent family

Date of the actual completion of the international search

7 November 2002

Date of mailing of the international search report

26/11/2002

Name and mailing address of the ISA

European Patent Office, P.O. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Glanddier, A

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IN 02/00058

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 362 378 A (YOSHINO KATSUMI ;KOMATSU MFG CO LTD (JP)) 11 April 1990 (1990-04-11) claim 1  -----	1-8

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IN 02/00058

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5567356	A	22-10-1996	AT 193708 T	15-06-2000
			AU 4152996 A	31-05-1996
			CA 2204653 A1	17-05-1996
			DE 69517444 D1	13-07-2000
			DE 69517444 T2	18-01-2001
			DK 796283 T3	07-08-2000
			EP 0796283 A1	24-09-1997
			ES 2146787 T3	16-08-2000
			FI 971954 A	25-06-1997
			GR 3034223 T3	29-12-2000
			JP 10509751 T	22-09-1998
			NO 972084 A	04-07-1997
			WO 9614343 A1	17-05-1996
			US 5863465 A	26-01-1999
US 5276112	A	04-01-1994	WO 9309175 A1	13-05-1993
			US 5519111 A	21-05-1996
WO 9322775	A	11-11-1993	WO 9322775 A1	11-11-1993
EP 0579027	A	19-01-1994	EP 0579027 A1	19-01-1994
			JP 3275061 B2	15-04-2002
			JP 6306280 A	01-11-1994
			JP 2002179911 A	26-06-2002
			US 5578249 A	26-11-1996
EP 0362378	A	11-04-1990	JP 2098461 C	02-10-1996
			JP 8002961 B	17-01-1996
			JP 63270734 A	08-11-1988
			EP 0362378 A1	11-04-1990
			WO 8808435 A1	03-11-1988